United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S4-81-017 Jan. 1982

EPA

Project Summary

Development of Analytical Test Procedures for Organic Pollutants in Wastewater—Application to Pesticides

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Test procedures were developed for monitoring concentrations of 58 pesticides in industrial discharge wastewater. The procedures involved: (a) solvent extraction, (b) extract concentration, (c) adsorbent column cleanup, and (d) gas or high pressure liquid chromatographic determination. The procedures were developed and evaluated using relevant industrial wastewater. Based on the results of this project, methods have been written and are available from EPA.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Clean Water Act of 1977, Section 304(h), stimulated research on analytical procedures for monitoring toxic compounds in industrial and municipal wastewater discharges. Pesticides are an important group of toxic compounds which have come under scrutiny for control by the National Pollutant Discharge Elimination System (NPDES) permits program. The purpose of this project was to develop procedures for a select group of pesticide compounds. Objectives were to minimize the cost of performing the analysis and maximize the probability of obtaining accurate results.

Method Development and Validation

In order to minimize the cost of performing the analysis, three ideas were incorporated in the philosophical approach to the method development: (a) multiresidue methods, wherein several compounds may be determined by one analysis, were favored, (b) standard analytical techniques and instruments, in common use, were incorporated in the methods, and (c) techniques used in approved EPA procedures were favored because of their future side-by-side use with these pesticide methods.

Preliminary development work utilized diluted standard reference materials for chromatography and cleanup studies and spiked distilled water for extraction recovery work. Then, samples of wastewater from pesticide manufacturing plants were subjected to the respective preliminary methods to test the method validity with relevant sample matrices. Aspects of the methods were altered if acceptable recovery and selectivity were not obtained. Sucoessful methods were assigned a prelimi-

nary EPA method number, written in EPA format, and scheduled for proposal use under the NPDES program.

Generally all the final methods used the same procedure. A 1-liter water sample near pH 7 was extracted three times with 60 mL of methylene chloride. The extracts were combined, dried by anhydrous Na_2SO_4, and concentrated by Kuderna-Danish (K-D) technique. After the solvent was exchanged into hexane and reduced to less than 100 mL by K-D, the extract was cleaned up by solid adsorbent chromatography in a glass column. The column effluent was concentrated by K-D, then analyzed by gas chromatography or high pressure liquid chromatography using selective detectors when possible. Exceptions were dinoseb which was extracted at pH 2, benomyl which was hydrolyzed to carbendazime by addition of 10 mL of concentrated HCl and stirring of the sample overnight prior to extraction, and aldicarb which was oxidized to the sulfone with peracetic acid prior to extraction.

Table 1 is an outline of much of the pertinent analytical information from the developed methods. More detail may be found in the report available from NTIS or the methods available from EPA.

Table 1. Pesticide Method Details

		Chromatography					
Method[a]	*Compound*	*Cleanup*[b]	*Column*[c]	*Detector*[d]	*Parameter*	*DL*[e] *µg/L*	*Wastewater*[f] *Recovery (%)*
604 Addendum	*Dinoseb*	–	*1*	*FID*	*160°C*	*20*	*82*
608 Addendum	*Chlorobenzilate*	*1*	*3*	*ECD*	*215°C*	*0.001*	*91*
	Chloroneb	*1*	*2*	*ECD*	*150°C*	*0.001*	*68*
	Chloropropylate	*1*	*3*	*ECD*	*215°C*	*0.001*	*130*
	Dibromochloropropane	*1*	*3*	*ECD*	*100°C*	*0.001*	*67*
	Etridiazole	*1*	*3*	*ECD*	*140°C*	*0.003*	*97*
	PCNB	*1*	*3*	*ECD*	*160°C*	*0.02*	*N/A*
619	*Ametryn*	*2*	*4*	*TSD*	*200°C*	*0.06*	*111*
	Atrazine	*2*	*4*	*TSD*	*200°C*	*0.03*	*122*
	Prometon	*2*	*4*	*TSD*	*200°C*	*0.03*	*119*
	Prometryn	*2*	*4*	*TSD*	*200°C*	*0.03*	*93*
	Propazine	*2*	*4*	*TSD*	*200°C*	*0.03*	*103*
	Simetryn	*2*	*4*	*TSD*	*200°C*	*0.07*	*182*
	Simazine	*2*	*4*	*TSD*	*200°C*	*0.05*	*106*
	Terbuthylazine	*2*	*4*	*TSD*	*200°C*	*0.03*	*107*
	Terbutryn	*2*	*4*	*TSD*	*200°C*	*0.05*	*102*
622	*Azinphosmethyl*	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*1.5*	*90*
	Bolstar	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.15*	*92*
	Coumaphos	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*1.5*	*213*
	Demeton-O	–	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.25*	*82*
	Demeton-S	–	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.25*	*17*
	Disulfoton	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.20*	*114*
	Fensulfothion	–	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*1.5*	*95*
	Fenthion	–	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.1*	*46*
	Phorate	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.15*	*58*
	Trichloronate	*1*	*5*	*FPD*	*150 to 220°C*[g] *at 25°C/min*	*0.15*	*42*
	Chlorpyrifos	*1*	*5*	*FPD*	*160 to 220°C at 25°C/min*	*0.3*	*96*
	Ronnel	*1*	*5*	*FPD*	*160 to 220°C at 25°C/min*	*0.3*	*75*
	Stirofos	*1*	*5*	*FPD*	*170 to 220°C at 20°C/min*	*0.5*	*112*
	Naled	–	*5*	*FPD*	*170 to 220°C at 20°C/min*	*0.5*	*81*

Table 1. (Continued)

Method[a]	Compound	Chromatography* Cleanup[b]	Column[c]	Detector[d]	Parameter	DL[e] µg/l	Wastewater[f] Recovery (%)
	Mevinphos	-	5	FPD	170 to 220°C at 20°C/min	0.3	94
	Dichlorvos	-	5	FPD	170 to 220°C at 20°C/min	0.1	107
	Diazinon	1	5	FPD	190°C	0.8	116
	Ethoprop	1	5	FPD	190°C	0.03	
	Parathion, methyl	1	5	FPD	190°C	0.8	79
623	MOCA	-	6	TSD	260°C	1.0	67
628	Carbofuran	1	7	HPLC-UV	CH_3CN/H_2O	5	114
629	Cyanazine	1	7	HPLC-UV	CH_3OH/H_2O	6	
631	Carbendazin	3	7	HPLC-UV	CH_3OH/H_2O	3	129
	Benomyl	3	7	HPLC-UV	CH_3OH/H_2O	3	
632	Duiron	3	7	HPLC-UV	CH_3CN/H_2O	0.3	128
	Fluometuron	1	7	HPLC-UV	CH_3CN/H_2O	0.5	85
	Linuron	3	7	HPLC-UV	CH_3CN/H_2O	0.3	74
	Methomyl	3	7	HPLC-UV	CH_3CN/H_2O	3.5	108
	Oxyamyl	3	7	HPLC-UV	CH_3OH/H_2O	1.5	95
	Propachlor	6	7	HPLC-UV	CH_3CH/H_2O	16	78
	Propoxur	1	7	HPLC-UV	CH_3CH/H_2O	16	67
633	Bromacil	5	9	TSD	210-250°C at 10°C/min	0.2	106
	Hexazinone	4	9	TSD	210-250°C at 10°C/min	0.5	106
	Terbacil	5	9	TSD	210-250°C at 10°C/min	0.5	99
	Metribuzin	4	8	TSD	240°C	0.7	53
	Triadimefon	4	8	TSD	240°C	0.7	83
	DEET	4	8	TSD	180°C	0.1	107
	Tricyclazole	4	9	TSD	240°C	0.1	87
*	Piperonyl butoxide	3	7	HPLC-UV	CH_3CN/H_2O	6	99[h]
*	Tokuthion	1	5	FPD	150 to 220°C[g]	0.5	40[h]
*	Piperalin	-	10	TSD	200°C	0.3	79
*	Aldicarb	3	4	TSD	150°C	0.4	46

[a] *EPA preliminary method number; methods available from EMSL, Cincinnati, OH 45268.*
[b] *Cleanup methods used: (1) Florisil adsorbent ethel ether (ee)/petroleum ether (pe) solvent, (2) alumina-10% deactivated, ee/pe solvent, (3) Florisil, acetone/hexane solvent, (4) Florisil-2% deactivated, acetone/hexane solvent, (5) Florisil-5% deactivated, acetone/hexane solvent, and (6) Florisil-20% ether/hexane, then acetone/hexane.*
[c] *Chromatography column: (1) 1% SP-1240DA, (2) 1% SP-2250, (3) 1.5% SP-2250/1.95% SP-2401, (4) 5% Carbowax 20M TPA, (5) 5% SP-2401, (6) 3% SP-2250-DB, (7) µ Bondapak C_{18}, (8) 3% SP-2401, (9) 3% SP-2250 DB, and (10) 3% SP-2340.*
[d] *Detector: FID = flame ionization, ECD = electron capture, TSD = thermionic nitrogen selective, FPD = flame photometric, UV = ultraviolet.*
[e] *DL = detection limit estimate.*
[f] *Average of four analyses.*
[g] *One meter column.*
[h] *Average of six analyses.*
* *Method number to be assigned.*

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The complete report, entitled "Development of Analytical Test Procedures for Organic Pollutants in Wastewater—Application to Pesticides," (Order No. PB 81-172 629; Cost: $10.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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